Organics on TiO_2 Surfaces: Extreme Charge Transfer Phenomena, On-surface Reactions, Barrier Heights of Formation and STM Imaging

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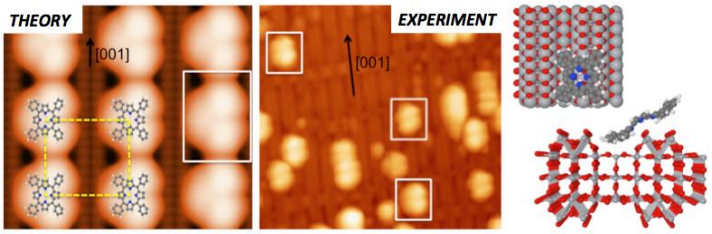
Understanding the interaction between organic molecules and surfaces is of paramount importance in diverse fields such as organic and molecular electronics, catalysis, and on-surface chemistry, among others. In particular, the growing field of organic electronics relies on the use of organic conjugated molecules as components of multilayer devices. To this aim, surfaces of titanium dioxide provide suitable conditions for the use of surface experimental techniques (ultra-high vacuum XPS, UPS, NEXAFS and STM) and their adequate combination with first-principles based calculations. TiO_2(110) surfaces provide an anisotropic template consisting of alternating bridging oxygen rows and 5-fold coordinated Ti_4^+ rows, making possible different adsorption geometries for different organic molecules. On this basis, the Unified IDIS model, a beyond-DFT many-body approach, and an accurate Keldish-Green-based theoretical scanning tunneling microscopy formalism have been recently used to fully characterize the interaction between a large variety of organic molecules – such as TCNQ, $C_{60}H_{30}$, Perylene, PTCDA, C_{60}, 2HTPP, NiTPP and ZnTPP – and TiO_2 surfaces. These molecules are prototypical electron donors and acceptors, and are in potentials of catalysis and molecular electronics as active catalysts precursors, promising candidates of organic conductors, and some of them interesting due to their hole-injection barrier recently evidenced. Within this contribution we will deeply analyze the interaction between TCNQ[1a] and perylene[1b] on the TiO_2(110)-1×1 surface, the on-surface (cyclo-)dehydrogenation reaction of $C_{60}H_{30}$ on the TiO_2(110)-1×1 surface,[2] recently discovered new C_{60}/TiO_2(110) and PTCDA/TiO_2(110) phases,[3a,3b] and the complex on-surface metalation process from 2HTPP towards NiTPP and ZnTPP on the 1×1 and 1×2 TiO_2(110) surfaces.[4a,4b]



Theoretical and experimental STM images of 2HTPP on the TiO_2(110)-1×2 surface

References

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